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Importance of interatomic hole screening in core-level spectroscopy of transition metal oxides: Mn 3*s* hole states in MnO

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Ab initio theoretical results are reported to determine the role of interatomic screening of the metal core hole in Mn 3*s* x-ray photoelectron spectra (XPS) of MnO. We present information that finally resolves the controversy about the relative importance of intra-atomic and interatomic effects to the XPS spectra of ionic manganese compounds. We focus on the transitions to high-spin 3*s* core hole states, using a nonorthogonal configuration interaction method. This method allows for a balanced treatment of configurations that involve different degrees of screening of the core hole. The differences between MnO and NiO are analyzed. Although at first glance the two XPS spectra seem to have similar features, the 3*s* hole final states have completely different characteristics. In MnO, interatomic screening of the core hole is found to play a minor role. This is in contrast with NiO, where the inclusion of interatomic screening of the metal core hole has been shown to be crucial for a proper explanation of the Ni 3*s* XPS. The main reason for the difference is an essentially atomic effect, namely the smaller electron affinity of Mn as compared to Ni. We have assigned the weak feature observed in the Mn 3*s* XPS spectrum of MnO at around 10 eV to be a charge-transfer-type high spin satellite.

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I. INTRODUCTION

Core-level ionizations, usually obtained with x-ray photoelectron spectroscopy (XPS),[1,2] and core-level excitations, especially to excited levels near the ionization limit,[3] can give valuable information about the electronic structure of matter. Spectroscopies based on these excitations have been applied to free atoms and molecules and to condensed matter. In this paper, we present information which resolves the ongoing controversy[4–10] about the relative importance of the contributions of intra-atomic and interatomic effects to the 3*s* level XPS of bulk MnO and other manganese compounds. For ionic transition metal (TM) compounds, especially TM oxides, the interpretation of the origin of features in the 2*p* and 3*s* level XPS is still a subject of active research; see, for example, Ref. 11 and references therein. Since there is strong evidence that the various mechanisms responsible for the XPS satellites have different importance in different TM systems,[11,12] we also compare the 3*s* XPS spectra of MnO with that of NiO.[13,14]

It was recognized some time ago[4] that the spin and spatial angular momentum coupling of the open core and the open *d* shell of the TM atom must be taken into account in order to explain the XPS spectra of TM materials. This coupling, often referred to as an exchange splitting (XS),[4] gives rise to final-state multiplets of different energies, each of which are reflected in the XPS spectra. The XS is particularly simple for 3*s* holes since the open $3s^1$ shell couples with the open *d* shell, which is Russell-Saunders coupled to the high spin multiplet ^{2S+1}L, to give only a ^{2S}L and a ^{2S+2}L final, ionic, state multiplet. In addition to the XS, there is a second intra-atomic effect which often makes important contributions to the 3*s* hole XPS spectra.[12,15] This is an electron correlation effect which involves configuration mixing or configuration interaction (CI) of the configurations formed by distributing the *M* shell electrons in all spin and spatial symmetry allowed ways over the 3*s*, 3*p*, and 3*d* subshells. In particular for Mn^{2+}, the near degeneracy between the $3s^13p^63d^5$ and $3s^23p^43d^6$ configurations leads to strong mixing of these configurations in the 3*s* hole state wave functions.[15] It is this mixing which is the dominant mechanism responsible for the observed complex 3*s* level XPS satellite structure.[6,10,15,16] For Mn, this near degeneracy effect is only important for the low spin coupling of the $3s^1(^2S)$ and $3d^5(^6S)$ open shells to a total ionic state which has ^5S multiplicity; it does not occur for the states where the coupling of the open shells is to the high spin ^7S multiplicity. As we note below, this consideration explains why we have chosen to study only the high spin ^7S or, in the octahedral symmetry of bulk MnO, $^7A_{1g}$ ionic states. Intra-atomic near degeneracy effects are general and contribute to the *s* hole XPS spectra of several other TM atoms[12,17] as well as to their *p* hole spectra.[9,17,18]

In addition to these *intra-atomic* mechanisms, there may also be an *interatomic* mechanism related to charge transfer (CT) in TM oxides and other ionic compounds, where the CT is between the ligands and the core-ionized TM; see, for example, Ref. 20, and references therein. It is usual to describe this interatomic mechanism within a framework that neglects the outermost *s* and *p* orbitals of the TM atom and which also assumes an (orthogonal) basis of pure TM *d* and pure oxygen, or other ligand, 2*p* atomic orbitals. Here, the CT is from O(2*p*) to TM(*d*) and the resulting 3*s* hole CT configuration is commonly denoted $3s^1d^{n+1}\underline{L}$. For the $3s^2$ occupation, the $3d^{n+1}\underline{L}$ configuration is believed to have a much higher diagonal energy than the $3d^n$ ground state[19] and therefore these configurations will not contribute signifi-

cantly to the ground-state wave function. For the $3s^1$ occupation, on the other hand, the energy difference between the $3d^{n+1}\underline{L}$ and $3d^n$ configurations is much smaller and the $3d^{n+1}\underline{L}$ configuration may even lie lower in energy than $3d^n$. For this occupation, the $3d^{n+1}\underline{L}$ configuration may make substantial contributions to the XPS spectra. Indeed, it has been suggested[8] that configurations which involve transfer of two ligand p electrons to the TM(d) shell may also be important.

There is a clear physical logic for the greater importance of these CT configurations when there is a core hole in the TM cation than when the TM core shells are filled. The effective nuclear charge, $Z_{\rm eff}(3d)$, seen by the $3d$ electrons increases by nearly 1 when an electron is removed from one of the TM ion core shells.[11] The energy of an electron in the $3d$ shell depends on a term involving $Z^2_{\rm eff}(3d)$ plus additional d-d shell Coulomb and exchange terms which represent the interaction of the d electrons with each other. Thus the energy of the CT configurations, $3s^1 3d^{n+1}\underline{L}$ and $3s^1 3d^{n+2}\underline{L}^2$, will be lower with respect to the energy of the normal configuration, $3s^1 3d^n$, than is the case when the $3s$ occupation is $3s^2$. The changes in the value of the electron affinity of a TM ion for different TM's, especially when a core hole is present, also have consequences for the character of the final ionic, core hole, states. Bagus *et al.*[11] used the changes in the TM electron affinity to explain the differences of the relative energies of the CT and normal configurations for MnO and NiO. We will follow a similar reasoning in our comparison and analysis of the $3s$ XPS spectra for MnO and NiO. Finally, we note that Bagus and collaborators have given evidence that the extent and the character of CT contributions to the XPS spectra of TM oxides depend strongly on the particular TM.[11,20–22]

The Mn $3s$ XPS spectra of MnO (Refs. 16 and 23) is rather complex and extends over ~50 eV. The first, lowest binding energy (BE) peak has the largest intensity and is followed by an intense second peak at ~6 eV higher BE. Parmigiani and Sangaletti[23] report a very weak satellite at ~10 eV; both Refs. 16 and 23 report a broad satellite at ~15–30 eV and Kowalszyk *et al.*[16] report a weak satellite at ~50 eV. The XPS spectra of Kowalszyk *et al.* are consistent, for both energies and intensities, with the theoretical results obtained in Ref. 15. This theoretical analysis was based on a rigorous and accurate many-electron theoretical treatment, including near degeneracy electron correlation effects, for ionization of an isolated Mn^{2+} ion. Based on this work, it is now generally agreed that the first and second peak correspond to high and low spin coupled final states. Indeed, Hermsmeier *et al.*[10] used the different spin polarization of the first, high spin peak and of the second, low spin peak as an internal source of spin polarized electrons which they used to probe the antiferromagnetic properties of MnO. The body of early experimental[4] and theoretical[15] work for Mn ionic complexes was contradicted in the mid 1980s by Veal and Paulikas[5] who made an empirical analysis of CT effects in MnF_2. They assigned the first peak as arising from a state which was dominantly a CT configuration while the second peak arose from a state which was dominantly the normal, $3s^1 3d^n$ configuration.

There have been extensive theoretical and experimental studies related to the importance of CT effects in the core-level XPS spectra of Mn ionic materials and this work continues to the present.[24,25] Hermsmeier *et al.*[6] measured the photoemission spectra for the $3s$ and $3p$ levels of gas phase atomic Mn. They found that the atomic spectra were very similar to the XPS spectra for MnF_2 and MnO solids. Their observation gives strong experimental support that the XPS spectra for condensed phase Mn compounds arises primarily from intra-atomic effects, rather than from interatomic CT. Sangaletti *et al.*[22] and Parmigiani and Sangaletti[23] reported comparative studies of the XPS spectra of the cubic oxides from MnO through NiO. A principal conclusion of their work is that the contribution of CT effects to the core-level XPS depends strongly on the particular TM ion, with CT being much more important for NiO than for MnO. Bagus *et al.*[11] reached a similar conclusion from the *ab initio* model Hamiltonian study of the $3s$ XPS of MnO and NiO. In recent work, the metal $2p$ and $3p$ XPS spectra of MnO were studied with a fully relativistic, nonempirical treatment of the XPS energies and intensities of an *isolated* Mn^{2+} ion.[9] This work treated the atomic angular momentum coupling of the open-shell electrons and the relativistic spin-orbit splittings on an equal footing. The results of this study showed that these atomic effects in Mn^{2+} account for the main features observed in the $2p$ and $3p$ XPS of MnO. Overall, the theoretical and experimental work cited above lead to the conclusion that intra-atomic effects dominate the Mn core XPS spectra and that the contribution of CT effects in ionic Mn compounds is quite small. On the other hand, Veal and Paulikas[5] interpret the main $3s$ hole XPS peak in MnF_2 as being due to a final state that is dominated by the $3s^1 3d^6\underline{L}$ configuration. Okada and Kotani[8] concluded that in the core-level XPS spectra of Mn compounds the solid-state CT contributions are appreciable, especially for the satellite structure. This conclusion was based on the results of their parametrized empirical model Hamiltonian studies. Gweon *et al.*[7] made a systematic analysis of their $3s$ photoemission spectra of Mn and Fe dihalides and mono-oxides, using a parametrized cluster model. They concluded that the importance of CT depends on the electronegativity of the ligands. In fluorides they found very little effect of CT in the lower two peaks, whereas in chlorides these peaks have strongly mixed non-CT–CT character. In mono-oxides, they find the character of the first two peaks to be between fluorides and chlorides, although somewhat closer to chlorides.

We will consider a nonempirical treatment of CT effects in MnO in order to resolve the disagreement over the importance of CT effects. This study builds on previous analysis of the importance of CT effects in NiO, which showed that an accurate, nonempirical treatment of the electronic structure of an embedded NiO_6 cluster which included the possibility of ligand to Ni($3d$) CT was necessary to explain the $3s$ XPS spectra.[13,14] In their early study of NiO, Bagus *et al.*[21] used a conventional configuration interaction (CI) formalism, where a common set of orbitals was used to describe the normal, $3d^8$, and CT, $3d^9\underline{L}$, configurations. Their results for the high and low spin $3s$ hole states of the NiO_6 cluster provided a reasonable fit to both the energies and intensities of the ob-

served XPS spectra. In more recent work, the nonorthogonal CI (NOCI) method[26–28] has been used with a NiO_6 cluster to study the $3s$ level XPS spectra.[13,14] With this approach, optimized orbital representations for the CT configurations were obtained, improving the description of the final states. However, the interpretation of the character of the XPS peaks obtained with the traditional CI formalism[21] was not changed when the NOCI method was used.[13,14] For most of the $3s$ hole states in NiO, there is a substantial mixing of the $3d^8$ and $3d^9\underline{L}$ configurations; in particular, this mixing occurs for all states which have significant XPS intensity.[21] Thus it is not possible to describe the states as being either normal or CT ''states.'' For example, it is found[14,21] that the two lowest energy high spin $3s$ hole state wave functions have approximately equal d character.

There is strong theoretical and experimental evidence to support the fact that core hole screening through electron transfer is important for the Ni XPS spectrum of NiO, whereas it is much less important for the Mn spectra of MnO. However, the nonempirical theoretical models which have been used to treat the Mn XPS spectra have either been for atomic models[9,15] or have used a model Hamiltonian.[11] Thus it is important to treat the Mn $3s$ XPS spectrum of MnO, using a computational model that allows for a proper variational study of CT effects in order to check the previous assignments; this is the primary objective of the present work. It is especially interesting to compare the importance of CT from the nearest ligands with that found previously for the Ni $3s$ XPS hole states in NiO. This comparison allows also for a rigorous test of the findings of Bagus *et al.*,[11] who concluded from a model Hamiltonian study that the relative importance of ligand to metal CT decreases strongly in going from NiO to MnO because of a decrease of the electron affinity of the embedded TM cation.

In the present study of the Mn $3s$ XPS spectrum of MnO we limit ourselves to the high spin final states. This allows us to focus on properties related to CT screening and to neglect atomic correlation effects arising from redistribution of the $3s$, $3p$, and $3d$ electrons among these shells. The latter correlation effects are important for the low spin coupled $3s$ hole states of MnO, but not for the high spin coupled states considered here.[17] Our results allow us to identify the first high spin satellite in the spectrum. We used the same nonorthogonal configuration interaction (NOCI) method as employed for the interpretation of the metal $3s$ XPS spectrum of NiO,[13,14] because this method ensures a balanced treatment of the relative energies of configurations that involve different degrees of CT from O $2p$ to Mn $3d$. The NOCI wave functions were obtained for an MnO_6 cluster model of the crystal. Orbital sets are optimized separately for each configuration state function (CSF) used in the NOCI expansion. Orbital symmetry breaking, or localization, is allowed. This localization is important for configurations with open shells that have considerable O $2p$ character.[13] We consider $3s$ hole states of MnO as well as states with a $3s^2$ occupation. The $3s^2$ ground state is needed to compute the XPS intensities of the $3s$ hole states. To check the sensitivity of our results on the cluster size, calculations were also performed for a larger MnO_6Mg_{18} cluster, in which the outer Mn^{2+} ions are represented by simpler Mg^{2+} ions. The imbalance in the treatment of the cation nearest neighbors of the O ligands in the MnO_6 cluster may introduce artifacts,[29,36] especially for the absolute values of the core-level BE's. It is expected that any such artifacts will be avoided with the MnO_6Mg_{18} cluster which has an improved, more balanced representation of the local environment of the O^{2-} anions.

In the next section we describe the cluster model, the important electron configurations, and the self-consistent field (SCF) and NOCI wave functions that have been calculated. This section also contains technical details about the calculations. In Sec. III we describe the NOCI results including a comparison with XPS experimental data. In Sec. IV we summarize our conclusions.

II. METHOD

A. Material model

In an ideal ionic model MnO is formed from Mn^{2+} cations and O^{2-} anions. Bagus *et al.*[30] have shown that the ground state of MnO is well described by this ionic model. The number of d electrons associated with the Mn^{2+} cation is ~ 5.1 showing that only a small degree of Mn($3d$) to O($2p$) covalent bonding is present; to a good approximation, the atoms in MnO can be regarded as $+2$ and -2 ions. These ions have an environment with octahedral O_h symmetry. Due to the O_h site symmetry, the Mn $3d$ shell splits into t_{2g} and e_g, with the t_{2g} electrons more strongly bound. The Mn^{2+} ground-state valence configuration is $t_{2g}^3 e_g^2$. These d electrons are coupled high spin to ${}^6A_{1g}$ symmetry in the O_h point group. If a $3s$ electron is ionized, the open shell configuration is $a_{1g}^1 t_{2g}^3 e_g^2$. The XPS dipole allowed final states have ${}^7A_{1g}$ or ${}^5A_{1g}$ symmetries. In an ionic model the final-state configuration is $3s^1({}^2A_{1g})3d^5({}^6A_{1g})$, exchange split into ${}^7A_{1g}$ and ${}^5A_{1g}$ multiplets. As noted before, we consider in the present study only the ${}^7A_{1g}$ $3s$ hole states and we focus on studying the importance of CT effects for these high spin final states.

The material model of condensed MnO which has been used for most of the present work is a cluster with a central manganese ion and its six oxygen nearest neighbors. This is the simplest cluster model in which the possible effects of low-lying CT excitations can be incorporated. Given the dominantly ionic character of MnO,[30] the net charge for this cluster is $10-$ and it is denoted by either the symbols MnO_6 or $[MnO_6]^{10-}$. The $[MnO_6]^{10-}$ cluster is embedded in a set of 140 point charges, PC's, at lattice positions; the values of the PC's were optimized by Broer *et al.*[31] to reproduce the Madelung potential due to an ideal rocksalt lattice of point charges. The manganese-oxygen distance of 4.200 bohr is taken from the bulk crystal.[32] The calculations are performed with the SYMOL-GNOME quantum chemistry program package.[33,34]

We also report results for a larger cluster model where the PC's nearest to the O^{2-} anions have been replaced by Mg^{2+} cations so that the O's are surrounded by the extended charge distributions of real atoms to represent its nearest neighbors. This cluster is $[MnO_6Mg_{18}]^{26+}$. It was used to test if the

actual environment of extended charge distributions, as occurs in the MnO crystal, would change the results obtained with the PC environment of the minimal $[MnO_6]^{10^-}$ cluster. For this minimal cluster, the environment of the O anions is imbalanced in that they have only one nearest-neighbor Mn cation while their other five nearest Mn neighbors are approximated by PC's. Closed-shell Mg^{2+} ions are used to represent these nearest neighbors, rather than the real open-shell Mn^{2+} ions, because the former are much simpler to treat. Since the ionic radius of Mg^{2+} is only ~0.2 bohr smaller than that of Mn^{2+},[35] the use of the Mg^{2+} ions will provide a reasonable estimate for the effects of the Pauli repulsion and orbital relaxation connected with a shell of Mn^{2+} ions. This embedding approach is similar to that used by de Graaf *et al.*[36] However, it is important to point out that Mg^{2+} ions cannot include the modest Mn($3d$)-O($2p$) covalent bonding which is known to be present in MnO.[30]

The basis set used for Mn is based on Wachters' set[37] which was extended with two p exponents[38] and one d exponent.[39] We used the following contraction scheme: for the s exponents: 62111111, for the p exponents: 4211111, for the d exponents: 3111. Overall, a rather flexible (14s,11p,6d/8s,7p,4d) contracted Gaussian-type orbital (CGTO) basis set was used for Mn. For O, the same (9s,5p/4s,3p) basis was used as was employed in previous studies on metal oxides; see, for example, Ref. 14. The basis set used for Mg was a (12s,7p/5s,3p) set from Veillard.[40] The contraction scheme used was 81111 for the s exponents and 4111 for the p exponents. In comparison to the set given by Veillard, we added a diffuse p exponent of 0.21.

B. Electronic structure

The leading configuration of the ${}^6A_{1g}$ ground state of the $[MnO_6]^{10^-}$ cluster is[41] (cores) $1t_{2g}^6\, 2t_{2g}^3\, 3e_g^4\, 4e_g^2$. The closed shell $1t_{2g}$ and $3e_g$ orbitals have mostly O$2p$ character, while $2t_{2g}$ and $4e_g$ are mainly built from Mn $3d$ atomic orbitals. However, these orbitals also reflect the modest Mn($3d$) O($2p$) covalent bonding. Thus the closed-shell orbitals, $1t_{2g}$ and $3e_g$, have a small Mn($3d$) contribution which is bonding with the dominant O($2p$) character and the open-shell orbital $4e_g$ has a small antibonding O($2p$) contribution; see Ref. 30 for a graphical view of this covalent bonding.

It is common, especially in approaches which use model Hamiltonians, to treat the orbitals for ionic TM oxides as atomic cores plus pure TM(d) and pure O($2p$) orbitals.[8,11,22] This approximation neglects the overlap between the TM(d) and O($2p$) orbitals and it neglects the covalent bonding between them. However, in this approximation the transfer of one electron from the ligand to Mn going from a normal, d^n, to a CT, $d^{n+1}\underline{L}$, configuration is well defined. For nonempirical electronic structure calculations, where overlap and covalency are properly taken into account, it is often not a good approximation to describe orbitals as pure TM(d) or pure O($2p$). In order to retain, as nearly as possible, the concept of d^n and $d^{n+1}\underline{L}$ configurations within the framework of rigorous electronic structure theory, Bagus *et al.*[11] had to place constraints on the orbitals which they used. In the present work, the orbitals used for the d^n and $d^{n+1}\underline{L}$ manifolds are the optimum orbitals, obtained by solving self-consistent field Hartree-Fock equations for the respective configurations. In this case, especially when the TM $3s$ shell is ionized, the cluster orbitals involve substantial mixing of TM and O($2p$) character.[13,14] However, the effective d occupation for a $d^{n+1}\underline{L}$ configuration is greater than for the d^n configuration although the difference of the d occupations for these configurations is much less than one electron. Despite this limitation, we have chosen to follow common practice and distinguish the configurations by denoting them as d^n and $d^{n+1}\underline{L}$, but we keep in mind that the orbitals may often be far from pure TM d or ligand orbitals.

The simplest description of the MnO ground state with the filled $3s^2$ core uses only the leading configuration. A better description is obtained by allowing the many-electron wave function to be an optimized linear combination of the leading $3d^5$ configuration and $3d^6\underline{L}$ configurations. Two different excited $3d^6\underline{L}$-type configurations contain states with ${}^6A_{1g}$ symmetry, which may mix with the ${}^6A_{1g}$ states of the leading $3d^5$ configuration. They correspond to O $2p \rightarrow$ Mn d transitions of the type $3e_g \rightarrow 4e_g$ or $1t_{2g} \rightarrow 2t_{2g}$, respectively. The first excited configuration, $1t_{2g}^6 2t_{2g}^3 3e_g^3 4e_g^3$, has a hole in the $3e_g$ orbital, which has oxygen p_σ character (i.e., directed towards the metal), the second excited configuration, $1t_{2g}^5 2t_{2g}^4 3e_g^4 4e_g^2$, has a hole in the $1t_{2g}$ orbital that is mainly oxygen p_π (i.e., perpendicular to the oxygen-metal bond). These configurations are denoted as $3d^6\underline{L}_\sigma$ and $3d^6\underline{L}_\pi$. There are no other states within the $3d^5$ and $3d^6\underline{L}$ manifolds in which the electrons are coupled to ${}^6A_{1g}$. There are ${}^6A_{1g}$ multiplets which correspond to so-called double charge transfer configurations, $3d^7\underline{L}^2$. In our study we have not included $3d^7\underline{L}^2$ configurations because, as we show below, the single charge-transfer configuration $3d^6\underline{L}$ has only minor importance in the wave function for the ground state.

Next, we consider states where a Mn $3s$ electron has been removed and where the open-shell coupling is to high spin ions, ${}^7A_{1g}$. The discussion of the configurations used for the NOCI wave functions for these states parallels that for the $3s^2$ case considered above. In a model without charge transfer, the configuration $\cdots 3s^1 \cdots 1t_{2g}^6 2t_{2g}^3 3e_g^4 4e_g^2$ would be expected to receive essentially all the XPS intensity for Mn $3s$ ionization. As for the ground ${}^6A_{1g}$ state, there are two, and only two, different excited $3s^1 3d^6\underline{L}$-type configurations which couple to ${}^7A_{1g}$ and hence mix with the $3s^1 3d^5$ configuration. These configurations are denoted as $3d^6\underline{L}_\sigma$ and $3d^6\underline{L}_\pi$ or, if there is a need to specify the $3s$ shell occupation, as $3s^1 3d^6\underline{L}_\sigma$ and $3s^1 3d^6\underline{L}_\pi$. The ${}^7A_{1g}$ configurations arising from the $3s^1 3d^7\underline{L}^2$ manifold are neglected. As for the ground state, our results indicate that the mixing of $3s^1 3d^6\underline{L}$ CT configurations with the normal $3s^1 3d^5$ configuration is small, thus the effect of $3s^1 3d^7\underline{L}^2$ on the lowest energy $3s$ hole state is expected to be even smaller.

C. Nonorthogonal configuration interaction

Our NOCI wave functions include the mixing of the $3d^5$, $3d^6\underline{L}_\sigma$, and $3d^6\underline{L}_\pi$ configurations. While, as discussed in the Introduction, this mixing is expected to be more impor-

tant for hole states with $3s^1$ occupation than for the ground state with $3s^2$ occupation, it has been included in both the ionized and ground states.

The ${}^6A_{1g}$ ground-state wave function and ${}^7A_{1g}$ $3s$ hole state wave functions that are used for the analysis of the Mn $3s$ XPS spectrum are obtained from a CI in terms of CSF's for $3d^5$-, $3d^6\underline{L}_\sigma$-, and $3d^6\underline{L}_\pi$-type configurations. The CSF's are each expressed in their own orbital set, which was optimized in a spin-restricted open-shell Hartree-Fock calculation. In a conventional spin- and symmetry-restricted Hartree-Fock scheme the $3d^6\underline{L}$-type configurations have an electron hole in an O($2p$) orbital which is delocalized over all six equivalent O atoms. It is known[26–28,42] that in many cases an SCF wave function with a hole that is localized on only one of the symmetry equivalent atoms is energetically favored and gives a better first-order description. Such SCF wave functions with localized orbitals can be obtained by lowering the symmetry restrictions on the orbitals. In the present study, in computing the SCF wave functions, we used C_{4v} symmetry instead of O_h. This enables localization of the O-$2p$ hole on one ligand and full relaxation of the orbitals can occur. Wave functions of A_{1g} symmetry in O_h can be obtained by taking proper linear combinations of localized CSF's, each with the oxygen hole on a different ligand. These symmetry adapted functions, which we call symmetry projected CSF's, form the basis for our CI expansions of the various states of the MnO_6 cluster. The CSF's are expressed in terms of sets of molecular orbitals optimized separately for each particular configuration and the different sets are mutually nonorthogonal. The 3×3 CI over the symmetry adapted CSF's is a NOCI and the GNOME routines[43] were used for an efficient evaluation of the overlap and Hamiltonian matrix elements between the CSF's. The resulting NOCI wave functions are mutually orthogonal and noninteracting; we will use these ${}^6A_{1g}$ initial state and ${}^7A_{1g}$ final-state NOCI wave functions to study the role of CT excitations in the high spin wave functions and in the experimental spectrum. In order to demonstrate the importance of relaxing the symmetry constraints in the SCF orbital optimizations so that the electron hole can become localized, we compared these NOCI results with a NOCI where the orbitals were constrained to have O_h symmetry. With this constraint, the orbitals for holes on the O ligands are delocalized over all six oxygen ligands.

D. XPS intensities

The relative intensities of the XPS lines are calculated using the sudden approximation (SA).[44] In this approximation, the intensity of each $3s^1$ final state is proportional to the squared overlap between the final-state wave function and the corresponding "frozen" $3s^1$ wave function. This frozen $3s^1$ wave function is defined by the ground-state wave function in which a Mn $3s$ electron is removed without any further changes to the wave function. If we would describe the initial $3s^2$ and final $3s^1$ states each with one single CSF, we would obtain a theoretical $3s$ XPS spectrum containing two peaks, connected to transitions to two final states, a "high spin" ${}^7A_{1g}$ final state and a "low spin" ${}^5A_{1g}$ final state, respectively. If the same orbital set would be used to describe both the high spin and the low spin ionic CSF's, the relative intensities of the transitions are obtained from the ratios of the multiplicities of the ionic states, 7/5.[44] If the $3s^1$ states are each expressed in their own optimized orbital set, deviations from this ratio can occur because the overlap between the "frozen" $3s^1$ wave function and the relaxed $3s^1$ wave function may be different for the high and low spin $3s^1$ states. However, the deviation due to different orbitals for the high and low spin final, ionic states is not likely to be especially large. For the $1s$ level core ionizations of the paramagnetic molecules $O_2({}^3\Sigma^-)$ and NO(${}^2\Pi$), the changes of the SA intensities due to the separate orbital optimization for the different core hole spin couplings was checked.[45] The departures of the calculated SA intensity ratios from the multiplicity ratios were $\sim$15% for O_2 and $<$3% for NO. Further, there may be a nonzero overlap between the frozen $3s^1$ state and other, excited CSF's with a Mn $3s^1$ configuration. A consequence of this nonzero overlap is that intensity can be distributed over a number of final states and we could find multiple transitions with nonzero intensity. Such overlaps lead to satellites which are generally described as shake satellites.[1,44] If we allow for configuration mixing both in the initial and, in particular, in the final-state wave functions, we obtain an improved description, with intensity distributed over a number of final states with significant intensity related to the many-body character of the states.

III. RESULTS AND DISCUSSION

The relative energies of the initial Mn $3s^2$ configuration of the $[MnO_6]^{10^-}$ cluster are given in Table I (a). The column labeled $\Delta E_{\mathrm{SCF}}(C_{4v})$ shows the relative SCF energies, which were obtained using C_{4v} symmetry restrictions on the orbitals. The orbitals of the SCF ground-state wave function transform according to O_h symmetry, in spite of the lower symmetry restrictions used and therefore the symmetry of

TABLE I. Relative energies (in eV) for C_{4v} localized and C_{4v} symmetry projected SCF wave functions; energies are also given for the $3d^6\underline{L}$ configurations Schmidt orthogonalized to $3d^5$ and to each other. The zero for the energies is taken as the C_{4v} SCF energy for the $3d^5$ configuration. The overlaps for the symmetry projected $3d^6\underline{L}_\pi$ CSF are with the $3d^5$ and the $3d^6\underline{L}_\sigma$ CSF's, respectively. (a) Mn $3s^2$ states and (b) Mn $3s^1$ states. The energies for the three roots of the NOCI are also given.

	ΔE_{SCF} (C_{4v})	ΔE_{SP} (overlap)	ΔE_{orth}	NOCI	
(a)				Root	ΔE
$3s^2d^5$	0	0	0	1	−0.18
$3s^2d^6\underline{L}_\sigma$	11.78	11.79 (0.31)	12.45	2	11.88
$3s^2d^6\underline{L}_\pi$	11.01	12.26 (0.39; 0.04)	13.35	3	14.07
(b)					
$3s^1d^5$	0	0	0	1	−0.78
$3s^1d^6\underline{L}_\sigma$	6.20	7.59 (0.15)	7.10	2	5.92
$3s^1d^6\underline{L}_\pi$	4.91	7.88 (0.33; 0.07)	7.52	3	9.44

the ground-state SCF wave functions is $^6A_{1g}$ in O_h. The second and third rows of the column labeled $\Delta E_{\mathrm{SCF}}(C_{4v})$ show the symmetry-broken SCF energies for the $3s^2d^6\underline{L}_\sigma$ and $3s^2d^6\underline{L}_\pi$ configurations, which have $^6A_1$ symmetry in C_{4v}. The open-shell orbital is mainly O $2p$ at one of the ligands. Since the three SCF wave functions are obtained without restricting them to be orthogonal to one another, they have mutual overlaps. We shall discuss these overlaps further in connection with the symmetry projected CSF's considered next. The next column of Table I (a) shows the energies of the symmetry projected $3s^23d^6\underline{L}$ CSF's, ΔE_{SP}. These CSF's have $^6A_{1g}$ symmetry in O_h. The overlaps of the symmetry projected $3s^23d^6\underline{L}_\sigma$ CSF and $3s^23d^6\underline{L}_\pi$ CSF with the $3s^23d^5$ and the overlap of the $3s^23d^6\underline{L}_\pi$ CSF with the $3d^6\underline{L}_\sigma$ CSF are shown in parentheses. It is important to note that the relative SCF energies and symmetry-projected energies of the $3d^6\underline{L}$ configurations have only a very limited meaning because of the considerable mutual overlaps. The column labeled ΔE_{orth} shows the energies obtained after Schmidt orthogonalization of the symmetry projected CSF's. The order in the orthogonalization was $3d^5$, $3d^6\underline{L}_\sigma$, $3d^6\underline{L}_\pi$. Finally, the last column, labeled NOCI, shows the energies of the three different $^6A_{1g}$ roots of the NOCI. In all cases, the energies are given relative to the SCF energy of the $3d^5$ CSF, taken as zero. Similar results for the $3s^1$ CSF's and NOCI are given in Table I (b). For the $3s^1$ compared to the $3s^2$ CSF's, the energies of the $3d^6\underline{L}$ CSF's relative to the $3d^5$ CSF have decreased by $\sim$5 eV. As discussed in the Introduction, this lowering of the relative energies of the $3d^6\underline{L}$ CSF's is due to the larger effective charge for the Mn $3d$ shell, $Z_{\mathrm{eff}}(3d)$ when a $3s$ electron is removed.[11]

Once the CSF's have proper O_h symmetry, the ΔE_{SP} and ΔE_{orth} energies are higher for the $3d^6\underline{L}_\pi$ CSF than for the $3d^6\underline{L}_\sigma$ CSF, this is true both for $3s^2$ and $3s^1$ configurations. This order is consistent with the stronger binding energy of electrons in the nonbonding oxygen ($2p_\pi$) orbitals compared to the oxygen ($2p_\sigma$) orbitals. The configuration interaction between the $3s^23d^5$ and the $3s^23d^6\underline{L}$ $^6A_{1g}$ CSF's is not very strong while the configuration interaction between the $3s^13d^5$ and the $3s^13d^6\underline{L}$ $^7A_{1g}$ CSF's is more important. For the $3s^1$ states the difference between the energies of the lowest NOCI root and the highest root is larger, by 2.7 eV, than the energy difference between the orthogonalized, symmetry projected CSF's, ΔE_{orth}. Further, the energy of the lowest NOCI root is 0.8 eV below the energy of the $3d^5$ CSF. The analogous NOCI energy changes for the $3s^2$ case are much smaller; see Table I (a). For the lowest NOCI root, the small mixing of the $3d^6\underline{L}$ CSF's with the dominant $3d^5$ CSF is shown in the first rows of Tables II and III for the $3s^1$ and $3s^2$ states, respectively. The tables give the weights, or squares of the coefficients, of the symmetry projected, orthogonalized $3d^5$, $3d^6\underline{L}_\sigma$, and $3d^6\underline{L}_\pi$ CSF's in the NOCI wave functions; these are denoted C_i^2 where the subscript i indicates the root of interest.

For the $3s^1$ case, see Table II, the configuration mixing between $3s^13d^5$ and $3s^13d^6\underline{L}$ turns out to be quite small, and we can therefore characterize the first NOCI wave function as mainly $3s^13d^5$, and the second and third as dominantly $3s^13d^6\underline{L}$. For the $3s^2$ case, see Table III, the mixing between $3s^23d^5$ and $3s^23d^6\underline{L}$ is even less important. The $3d^6\underline{L}_\sigma$ and $3d^6\underline{L}_\pi$ CSF's do, however, show a large mixing among themselves, causing considerable separation between the NOCI energies of the second and third roots. For the $3s^2$ case this separation is 2.2 eV; it is significantly increased over the energy difference of the orthogonalized symmetry projected $3d^6\underline{L}$ CSF's which is 0.9 eV. The change is even larger for the $3s^1$ case where the NOCI energies of the second and third roots differ by 3.5 eV while the energies of the $3d^6\underline{L}$ symmetry projected CSF's differ by only 0.4 eV. Table II shows that the $3s^13d^6\underline{L}$ CSF's have about a 50% weight in each of the two higher NOCI roots. This large mixing explains the low SA I_{rel} for the second $3s^1$ NOCI root; see below. Table III shows that there is also a large mixing of the $3s^23d^6\underline{L}$ CSF's in each of the second and third NOCI roots.

TABLE II. Relative NOCI energies (in eV), composition, and relative intensities I_{rel} for the $^7A_{1g}$ $3s$ hole states. The composition is given as the square of the CI coefficients in terms of the symmetry projected, orthogonalized CSF's, C_i^2 for the ith NOCI root

	E_{rel} (eV)	$C_i^2(3s^13d^5)$	$C_i^2(3s^13d^6\underline{L}_\sigma)$	$C_i^2(3s^13d^6\underline{L}_\pi)$	L_{rel}
Ψ_1	0	0.923	0.056	0.021	1
Ψ_2	6.70	0.005	0.501	0.494	0.00
Ψ_3	10.22	0.072	0.442	0.485	0.09

The XPS relative intensities, I_{rel}, for the three NOCI $^7A_{1g}$ states, obtained within the sudden approximation,[44] are also shown in Table II. The I_{rel} are normalized so that $I_{\mathrm{rel}}=1$ for the lowest energy, dominantly $3d^5$, NOCI $^7A_{1g}$ $3s$ hole state. Almost all intensity corresponding to high spin final states goes into the first peak. The second $^7A_{1g}$ state at 6.7 eV gets essentially no intensity. The third state, at 10.2 eV, carries less than one-tenth of the intensity of the first transition. It can explain the weak satellite observed around 10 eV in the XPS spectrum.[23] The present results are also in agreement with the predictions of Bagus *et al.*[11] from a model Hamiltonian study, who also estimated CT-type excited states at about 10 eV.

It is interesting to compare the present results for MnO to those obtained with the same computational method by de Graaf and collaborators[13,14] for the $3s$ XPS spectrum of NiO. In NiO, the leading configuration is $3d^8$ and there is only one, instead of two, charge-transfer configuration, of the type $3d^9\underline{L}_\sigma$. There are therefore two, instead of three, high spin $3s$ hole states for the NOCI wave functions. They were both found to have significant charge-transfer character: the

TABLE III. Relative NOCI energies (in eV) and composition of the $(3s)^2$ states of $^6A_{1g}$ symmetry. For the composition, see the caption of Table II.

	E_{rel}	$C_i^2(3s^23d^5)$	$C_i^2(3s^23d^6\underline{L}_\sigma)$	$C_i^2(3s^23d^6\underline{L}_\pi)$
Ψ_1	0	0.988	0.005	0.008
Ψ_2	12.06	0.000	0.710	0.290
Ψ_3	14.25	0.012	0.285	0.702

TABLE IV. Hamilton matrix elements, in eV, for MnO and NiO between Schmidt orthogonalized symmetry projected CSF's. For all cases, the diagonal energies are relative to the energy of the d^n CSF taken as $H_{1,1}=0$. For NiO the off-diagonal matrix elements were computed using the data in Ref. 14. (a) Matrix elements between $^7A_{1g}$ CSF's, $\langle\Phi_a|H|\Phi_b\rangle$ for MnO, where the Φ are the $(3s)^1d^5$ and Schmidt orthogonalized symmetry projected $(3s)^1d^6\underline{L}_\sigma$ and $(3s)^1d^6\underline{L}_\pi$ CSF's, respectively. (b) Matrix elements between $^4A_{2g}$ CSF's, $\langle\Phi_a|H|\Phi_b\rangle$ for NiO, where the Φ are the $(3s)^1d^8$ and Schmidt orthogonalized symmetry projected $(3s)^1d^9\underline{L}_\sigma$ CSF's. (c) Matrix elements between $^6A_{1g}$ CSF's, $\langle\Phi_a|H|\Phi_b\rangle$ for MnO, where the Φ are the $(3s)^2d^5$ and Schmidt orthogonalized symmetry projected $(3s)^2d^6\underline{L}_\sigma$ and $(3s)^2d^6\underline{L}_\pi$ CSF's, respectively. (d) Matrix elements between $^3A_{2g}$ CSF's, $\langle\Phi_a|H|\Phi_b\rangle$ for NiO, where the Φ are the $(3s)^2d^8$ and Schmidt orthogonalized symmetry projected $(3s)^2d^9\underline{L}_\sigma$ CSF's.

(a) $(3s)^1$ states in MnO

	$3s^1d^5$	$3s^1d^6\underline{L}_\sigma$	$3s^1d^6\underline{L}_\pi$
$3s^1d^5$	0.0	2.15	1.60
$3s^1d^6\underline{L}_\sigma$	2.15	7.10	1.40
$3s^1d^6\underline{L}_\pi$	1.60	1.40	7.52

(b) $(3s)^1$ states in NiO

	$3s^1d^8$	$3s^1d^9\underline{L}_\sigma$
$3s^1d^8$	0.0	1.95
$3s^1d^9\underline{L}_\sigma$	1.95	4.14

(c) $(3s)^2$ states in MnO

	$3s^2d^5$	$3s^2d^6\underline{L}_\sigma$	$3s^2d^6\underline{L}_\pi$
$3s^2d^5$	0.0	0.94	1.26
$3s^2d^6\underline{L}_\sigma$	0.94	12.45	0.91
$3s^2d^6\underline{L}_\pi$	1.26	0.91	13.35

(d) $(3s)^2$ states in NiO

	$3s^2d^8$	$3s^2d^9\underline{L}_\sigma$
$3s^2d^8$	0.0	1.85
$3s^2d^9\underline{L}_\sigma$	1.85	11.94

weight of the symmetry projected, orthogonalized $3s^13d^9\underline{L}_\sigma$-type CSF was 0.14 in the first high spin final state and 0.86 in the second. In NiO the second high spin $3s$ hole state is 5.8 eV above the first, whereas in MnO the high spin $3s^13d^6\underline{L}$ states are at 6.7 and 10.2 eV above $3s^13d^5$. In NiO, the relative intensity corresponding to the second state was 0.17, i.e., almost twice as large as the relative intensity of 0.09 found for the third state in MnO, while the second NOCI MnO state carries no intensity. The difference between the satellite structure in the XPS spectra of MnO and NiO becomes clear when the Hamiltonian matrix elements between the $3s^13d^n$ SCF CSF and the symmetry projected, Schmidt orthogonalized $3s^13d^{n+1}\underline{L}$ CSF's are compared. These matrices are given in Table IV (a) and (b) for the cluster calculations on MnO and NiO, respectively. In Table IV (c) and (d), we also give the corresponding matrix elements for the initial $(3s)^2$ states of MnO and NiO; for the present, we focus on the matrix elements for the $(3s)^1$ configurations. The difference between the NOCI results obtained for NiO and MnO is mainly due to the larger energy separation between the $3d^n$-and $3d^{n+1}\underline{L}$-type configurations as pointed out earlier in Ref. 11. The off-diagonal Hamilton matrix elements are comparable, ~2 eV in both NiO and MnO. In MnO, however, the $3d^{n+1}\underline{L}$ CSF's are at ~7.3 eV above the $3d^n$ configuration, almost twice the separation found in NiO, viz. ~4.0 eV, explaining the weaker interaction between the configurations to give the final states in MnO as compared to NiO.

The difference in the separation between the $3d^n$ and $3d^{n+1}\underline{L}$ configurations in MnO and NiO is caused by the different electron affinity of the TM ions, which is only partly compensated for by the difference in Madelung potential. With our present calculations for MnO_6 and previous work[13,14] for NiO_6, we are able to compare individual contributions that provide an understanding of the different diagonal energies in the NOCI for these TM's and hence the different role of CT configurations. This is achieved by comparing the electron affinities (EA's), or electron addition energies, for adding an electron to the cation d shell and by comparing the O $2p$ ionization potentials (IP's) or ionization energies, between the MnO_6 and NiO_6 clusters. Because the calculations for these two clusters involved analogous basis sets and point charge embedding, it is numerically meaningful to compare the computed EA's and IP's between these clusters. For both the MnO_6 and NiO_6 clusters, we consider the EA for adding an electron to the open e_g shell and the IP for removing an electron from a localized O($2p$) orbital of σ character to form a $3d^n\underline{L}_\sigma$ configuration. These definitions are used for the EA's and IP's in order to have suitable comparisons between the two clusters since for NiO only excitations of e_g, or σ, character are possible. In Table V (a) the SCF EA's are given; the TM EA for NiO_6 is 4.5 eV larger than the EA for MnO_6. When the different Madelung potentials in NiO and MnO are taken into account, this EA difference is consistent with the 6.0-eV difference of the EA's for the isolated Mn^{2+} and Ni^{2+} ions.[11] The NiO lattice constant, $a_0=7.87$ bohrs, is shorter than the MnO $a_0=8.40$ bohrs.[32] This difference in lattice constants leads to a change in the Madelung potential energy at the metal cation site from -22.7 eV for MnO to -24.2 eV for NiO. The difference of the Madelung potential energies is -1.5 eV and it reduces the free ion EA difference from 6.0 eV to $6.0-1.5=4.5$ eV; this value is very close to the value for the EA difference directly calculated with the embedded clusters; see Table V (a). The IP's of the O $2p_\sigma$ electrons, computed with the ΔSCF method,[46] are given in Table V (b). The IP is 1.5 eV smaller in MnO_6, mainly due to the weaker Madelung potential at the oxygen sites in MnO. Assuming the interaction between the ligand hole and the extra TM d electron to be similar in MnO and NiO, we expect the $3d^{n+1}\underline{L}-3d^n$ energy difference in MnO_6 to be $4.5-1.5=3$ eV larger than in NiO_6. This accounts well for the difference of around 3 eV we obtained for the orthogonalized $d^{n+1}\underline{L}$-type states, reported in Table IV.

The results in Table IV (a) and (b) also explain the character of the second and third roots of the NOCI for the $3s^1$ states which are given in Table II. Note that the diagonal

TABLE V. Electron affinities and ionization potentials for $3s$ hole states of $[MnO_6]^{10-}$ and $[NiO_6]^{10-}$ clusters. (a) Electron affinities. ΔSCF results obtained using O_h symmetry for the clusters. (b) Ionization potentials. ΔSCF results, obtained using C_{4v} symmetry for the clusters. The valence hole orbital is localized on one of the oxygen ligands and has a_1 symmetry.

(a) Electron affinities	States (configurations)	Relative energy (eV)
$[MnO_6]$	$^7A_{1g}$ $(3s^1d^5)-{}^6E_g$ $(3s^1d^6)$	6.06
$[NiO_6]$	$^4A_{2g}$ $(3s^1d^8)-{}^3E_g$ $(3s^1d^9)$	10.53
(b) Ionization potentials	States (configurations)	Relative energy (eV)
$[MnO_6]$	$^7A_1$ $(3s^1d^5\underline{L}_\sigma)-{}^6A_1$ $(3s^1d^5)$	16.62
$[NiO_6]$	$^4B_1(3s^1d^8\underline{L}_\sigma)-{}^3B_1(3s^1d^8)$	18.14

matrix elements of the $3d^6\underline{L}_\sigma$ and $3d^6\underline{L}_\pi$ orthogonalized, symmetry projected CSF's are nearly the same. It is possible to transform the Hamiltonian matrix to a new basis of Ψ_- and Ψ_+ which are given by $\Psi_-=[3d^6\underline{L}_\sigma-3d^6\underline{L}_\pi]/\sqrt{2}$ and $\Psi_+=[3d^6\underline{L}_\sigma+3d^6\underline{L}_\pi]/\sqrt{2}$. With this transformation, the diagonal H matrix elements are $H_{-,-}\approx 6$ eV and $H_{+,+}\approx 9$ eV. These values are close to the NOCI eigenvalues for the second and third roots, see Table I (b). The near equality of these diagonal matrix elements with the eigenvalues suggests that the second and third NOCI roots are dominated by Ψ_- and Ψ_+, respectively. One reason for this dominance is that the off-diagonal matrix element, $H_{+,-}$, is quite small; $|H_{+,-}|\approx 0.2$ eV. Because this off-diagonal matrix element is small, the $3d^6\underline{L}_\sigma$ and $3d^6\underline{L}_\pi$ CSF's should have roughly equal weights in the second and third NOCI eigenvectors; this is, indeed, the case as shown by the results in Table II. Finally, the off-diagonal matrix element connecting Ψ_- with the $3s^13d^5$ CSF will be small because of the cancellation of the nearly equal off-diagonal matrix connecting $3s^13d^5$ with $3s^13d^6\underline{L}_\sigma$ and $3s^13d^6\underline{L}_\pi$ which are 2.15 and 1.60, respectively; see Table IV. This explains the very small mixing of the $3s^13d^5$ CSF in the second NOCI root; see Table II.

In order to show the importance of allowing the variational freedom for the orbitals to become localized, we also carried out NOCI calculations, where orbitals constrained to have O_h symmetry, were used for the $3d^6\underline{L}$ CSF's. Since the orbitals for the $3d^5$ CSF's retain O_h symmetry, even in the C_{4v} symmetry wave functions, there are no changes for these CSF's. The O_h symmetry constrained SCF orbitals were optimized for configurations with maximum spin, sextet for $3s^23d^6\underline{L}$ and septet for $3s^13d^6\underline{L}$ configurations. However, spatial symmetry was treated somewhat differently; the SCF orbitals were optimized for weighted averages, WA's, of the CSF's that can be formed with the particular open-shell, $3d^6\underline{L}$, configuration. For the $3d^6\underline{L}_\sigma$, or $t_{2g}^3e_g^3\underline{L}_\sigma$, configuration, the WA is over the energies of A_{1g}, A_{2g}, and E_g CSF's; for the $3d^6\underline{L}_\pi$, or $t_{2g}^4e_g^2\underline{L}_\pi$, configuration, the WA is over the energies of A_{1g}, E_g, T_{1g}, and T_{2g} CSF's. The orbitals for these WA's are used to construct A_{1g} CSF's for the NOCI calculation. The relative energies of the symmetrized CSF's obtained with these O_h symmetry adapted orbitals and the NOCI energies are given in Table VI.

For the $3s^1$ NOCI states of MnO, there are large effects on the second and third roots depending on whether O_h or C_{4v} symmetry constraints are used for the orbitals. The energy splitting of these roots is 3.5 eV when C_{4v} localized orbitals are used for the NOCI but only 1.2 eV when symmetry constrained O_h orbitals are used; see Tables 1 (b) and VI (b). Furthermore, the strongest XPS SA relative intensity into this manifold of states is reduced by almost a factor of 2 from 0.09 to 0.05. However, since the intensity is small with either C_{4v} or O_h orbitals, the relatively large changes between the NOCI results for these two cases lead to only small changes in the predicted MnO XPS spectra. Not surprisingly, this is another consequence of the small mixing of the normal and CT CSF's for the core ionized states of MnO and of the small XPS intensity carried by the dominantly CT excited core hole states.

The precise values of the CI mixing coefficients of the $3s^13d^5$ and $3s^13d^6\underline{L}$ configurations depend on the orbital basis used to describe the various configurations. In our approach, all orbitals are optimized by using the variational principle to determine the best orbitals for each configuration. The orbital relaxation, which we take fully into account, may include both intra-atomic orbital contraction and extra-atomic screening. This has a considerable advantage over semiempirical approaches[7,8] since these approaches do not explicitly treat the intra-atomic contractions and hence they must make approximations about the consequences of these contractions for the matrix elements. For example, Okada

TABLE VI. Relative energies (eV) of the orthogonalized, symmetry projected CSF's, and the NOCI states for MnO_6 using SCF orbitals obtained with O_h symmetry constraints. For the $3s^1$ states the relative SA intensities I_{rel} are also given.

	$\Delta E(^6A_{1g})_{orthog}$	$^6A_{1g}$	NOCI	I_{rel}
a.		Root	ΔE	
$3s^2d^5$	0	1	−0.04	
$3s^2d^6\underline{L}_\sigma$	15.15	2	15.03	
$3s^2d^6\underline{L}_\pi$	15.37	3	15.63	
b.	$E(^7A_{1g})_{orthog}$	$^7A_{1g}$	NOCI	
$3s^1d^5$	0	1	−0.17	1
$3s^1d^6\underline{L}_\sigma$	9.74	2	10.24	0.00
$3s^1d^6\underline{L}_\pi$	9.40	3	9.07	0.05

TABLE VII. Relative SCF energies, in eV, and overlap integrals (in parentheses) of initial $3s^2$ and final $3s^1$ states, obtained with O_h symmetry constraints, for embedded MnO_6 and MnO_6Mg_{18} clusters. WA: weighted average of all states with maximum spin: $^6A_{1g}$, $^6A_{2g}$, and ^6E_g for $3s^2d^6\underline{L}_\sigma$; $^6A_{1g}$, ^6E_g, $^6T_{1g}$, and $^6T_{2g}$ for $3s^2d^6\underline{L}_\pi$; $^7A_{1g}$, $^7A_{2g}$, and ^7E_g for $3s^1d^6\underline{L}_\sigma$; $^7A_{1g}$, ^7E_g, $^7T_{1g}$, and $^7T_{2g}$ for $3s^1d^6\underline{L}_\pi$.

$\Delta E(\mathrm{WA})_{\mathrm{SCF}}$ (overlap)	MnO_6	MnO_6Mg_{18}
$3s^2d^5$	0	0
$3s^2d^6\underline{L}_\sigma$	14.47 (0.14)	14.37 (0.15)
$3s^2d^6\underline{L}_\pi$	15.28 (0.03; 0.00)	14.55 (0.03; 0.00)
$3s^1d^5$	0	0
$3s^1d^6\underline{L}_\sigma$	8.44 (0.21)	8.47 (0.22)
$3s^1d^6\underline{L}_\pi$	9.16 (0.05; 0.00)	8.73 (0.05; 0.00)

and Kotani[8] assume that the off-diagonal matrix elements between the d^n and $d^{n+1}\underline{L}$ configurations are independent of whether a core hole is present of not. As can be seen from Table IV (a) and (c), this assumption does not appear to hold for MnO. The off-diagonal matrix elements connecting the $d^6\underline{L}$ configurations with the d^5 configuration are 1.3 and 2.3 times larger when a $3s$ hole is present than for the $(3s)^2$ case. On the other hand, for NiO, Table IV (b) and (d), the matrix element connecting $3s^13d^8$ and $3s^13d^9\underline{L}$ is only 5% larger than the matrix element connecting $3s^23d^8$ and $3s^23d^9\underline{L}$. As we noted earlier, the matrix elements for our *ab initio* calculation are not strictly comparable to the semiempirically adjusted matrix elements used in model Hamiltonian calculations.[7,8] However, the changes in the off-diagonal matrix elements, described above, for MnO raise questions about the validity of the assumption that these matrix elements can be assumed constant.

To check the dependence of our results on the size of the cluster used to represent MnO, we performed calculations for a larger, MnO_6Mg_{18}, cluster. Here the second shell of cations that surround the O anions of the MnO_6 cluster are represented by Mg cations rather than point charges. This cluster is chosen to represent, with a computationally tractable model, the extended charge distribution of the Mn cations present in the real material; see Sec. II A for further details.

For the MnO_6Mg_{18} cluster SCF calculations for the orbitals were carried out with O_h symmetry constraints, for high spin couplings to either sextet or septet for the $3s^2$ and $3s^1$ case, respectively. For the $3d^5$ configurations of both the $3s^2$ and $3s^1$ cases, the SCF energy and orbitals were for states that had proper A_{1g} spatial symmetry. However, for the $3d^6\underline{L}_\sigma$ and $3d^6\underline{L}_\pi$ configurations, the SCF energies and orbitals were for WA's over the different spatial symmetries possible for the open-shell CSF's, see above. The overlaps between proper symmetry adapted SCF wave functions for the MnO_6Mg_{18} clusters were also evaluated. In Table VII we compare the WA SCF energies and the CSF overlap of the $3d^5$, $3d^6\underline{L}_\sigma$, and $3d^6\underline{L}_\pi$ configurations for the MnO_6Mg_{18} cluster with equivalent results for the smaller MnO_6 cluster. It is clear from Table VII that the energies and overlap integrals computed for the larger cluster are quite close to those obtained for the smaller cluster. This is an indication that relative energies and intensities may change somewhat, but there would not be drastic changes if a larger cluster were to be employed.

IV. CONCLUSIONS

Our main conclusion is that intra-atomic effects dominate the Mn $3s$ XPS spectra and that the contribution of CT effects is quite small. This is not in agreement with the conclusions reached by Veal and Paulikas,[5] Okada and Kotani,[8] and Gweon *et al.*[7] The conclusion of Veal and Paulikas[5] that the lowest energy Mn $3s$ hole state is best described by the configuration $3s^13d^5\underline{L}$ was made specifically for MnF_2, not for MnO. However, it is reasonable to assume that the physical mechanisms and characteristics that describe the dominant aspects of the spectra are rather similar for the two compounds. Okada and Kotani[8] as well as Gweon *et al.*[7] conclude that the lowest $3s$ hole state of MnO is mainly of $3s^13d^5$ character. However, Okada and Kotani[8] also conclude that CT effects are important for determining the character of the lowest state and of the higher energy satellites. The arguments of Gweon *et al.*[7] are that the importance of CT effects is different among MnF_2, MnO, and $MnCl_2$. They conclude that while the importance of CT for MnO is intermediate between MnF_2 and $MnCl_2$, CT configurations make a substantial contribution to the first, lowest energy, $3s$ hole state in MnO. None of these interpretations is consistent with the results of our *ab initio* study. On the contrary, we give strong and detailed *ab initio* evidence to support our conclusion that the contribution of CT effects in the $3s$ XPS spectra of MnO is small. However, our conclusions are in agreement with earlier work of Hermsmeier *et al.*,[6] Parmigiani and Sangaletti,[23] and Bagus *et al.*[11] The conclusion by Hermsmeier *et al.* is based primarily on the large similarities of the $3s$ hole spectra for isolated Mn atoms, for MnF_2, and for MnO. The conclusion of Parmigiani and Sangaletti[23] is based on a combination of Anderson model Hamiltonian treatments with XPS spectra. The conclusion of Bagus *et al.*[11] is based on an *ab initio* treatment within the theoretical framework of a model Hamiltonian. The present work extends, in an important way, these earlier treatments.[6,11,23]

We have reported results that take the effects of CT configurations into account in a fully relaxed variational treatment and without the introduction of any empirically adjusted parameters. In the prior theoretical treatments of Okada and Kotani,[8] Taguchi *et al.*,[47] and also of Gweon *et al.*,[7] adjustable parameters, describing the diagonal energies and off-diagonal matrix elements for CT configurations, have been fit to reproduce experimental results. Furthermore, in the prior work of Bagus *et al.*[11] on MnO, idealized CT configurations were used. While the matrix elements for these idealized configurations were computed rigorously, orbital relaxations and, in particular, orbital localizations were not taken into account. These effects have been properly treated in the present work. Our results provide full theoretical confirmation of the conclusion drawn from the experimental spectra for Mn compounds.

We have also discussed the different origins of the 3*s* hole spectra for MnO and NiO in terms of our theoretical treatments which include, in a balanced fashion, interatomic as well as intra-atomic effects. The different origins lead to 3*s* hole final states with completely different physical characteristics although at first glance the two XPS spectra seem to have similar features. In particular, the spectra for MnO and for NiO both contain an intense satellite peak at ~6 eV higher binding energy than the main XPS peak. In NiO, the main peak and the satellite are both assigned to high spin final states and they both have considerable charge transfer character. In MnO, the main line is assigned to a high spin final state, and it has negligible charge transfer character. The strong peak at ~6 eV higher binding energy in MnO cannot be assigned to a high spin final state. Instead, there is a weak satellite at ~10 eV that has been observed by Parmigiani and Sangaletti,[23] and our work assigns this satellite as arising from a final state with dominant CT character.

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